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VAPORIZATION FROM ALKALI CARBONATE MELTS

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ABSTRACT

This paper examines the processes responsible for fume generation in the kraft furnace. Sulfide oxidation produces nearly an order of magnitude more fume than strongly reducing conditions. Sodium hydroxide is not a highly volatile species in a sodium carbonate-sulfide melt. The lower than equilibrium enrichment factors for chloride and potassium in the kraft furnace are likely a result of fume dilution due to oxidation enhanced sodium vaporization. Sodium chloride vaporization from a sodium carbonate-sulfide-chloride melt during oxidation enhanced sodium vaporization is accurately described by Raoult's Law.

INTRODUCTION

One of the principal steps in the kraft pulping process is the recovery of the pulping chemicals. In the recovery furnace, black liquor from the pulping process is burned and the residual pulping chemicals are converted to alkali carbonate and sulfide. The burning of black liquor is considerably more complex than the burning of fossil fuels. The combustion process must be controlled to achieve both the combustion of the organic content of the black liquor and the reduction of the sulfur compounds present to sodium sulfide.

During the burning of the kraft black liquor, a large quantity of fume particles are generated from the vaporization and condensation of inorganic sodium and potassium compounds. These particles are typically 0.25 to 1.0 μm in diameter and are composed principally of sodium sulfate and sodium carbonate. Fume particles form deposits on the heat transfer surfaces, which reduce heat transfer rates, may eventually plug the gas passages, and may form a corrosive environment at the metal surface. Fume that does not deposit in the furnace is captured by an electrostatic precipitator, mixed with the black liquor, and recycled to the furnace.

Borg et al. (1) conducted a study of the origins of sulfur and sodium emissions from a kraft boiler. From electron microscopy studies, two types of particles were identified: those formed by entrainment and burning of black liquor droplets and those formed from vaporization of inorganic compounds in the lower furnace and condensation of these compounds in furnace gases. From the particle sizes it was determined that the weight percentage of actual carry-over (burnt liquor particles) was very small (less than 1 wt.% of the total

particles) compared to the fume particles. However, the location at which the particles were collected was not identified, and it is well known that carry-over particles, being heavier, tend to drop out of the gas stream before the precipitators. Rizhinshvili and Kaplun (2) also identified both types of particles. They found that the larger carry-over particles were nearly absent from the gas stream beyond the economizer.

POTASSIUM AND CHLORINE

Important nonprocess elements in the kraft process are potassium and chlorine. Keitanniemi and Virkola (3) found that the wood chips are a major source of potassium and chloride. Seawater transportation of logs can be a significant source of chloride. Karjalainen et al. (4) estimated that the sodium chloride input to a kraft mill from seaborne logs can be 45 lb of sodium chloride per ton of pulp. This is a relatively high level compared to a typical sodium sulfate makeup of 80 lb per ton of pulp. Relatively small amounts of chloride are also introduced into the recovery system with makeup chemicals. A potential source of chloride is the recovery of bleach plant effluent to eliminate a major source of water pollution. Karjalainen et al. (4) estimated that sodium chloride input from bleach plant effluent could be as high as 270 lb per o.d. ton of pulp.

Compared to Na_2CO_3 , potassium and chloride compounds such as NaCl and KCl are relatively volatile in the kraft furnace and the fume is enriched in these elements. Reeve et al. (5) reported potassium enrichment factors [the ratio of $\text{K}/(\text{Na}+\text{K})$ in the fume to $\text{K}/(\text{Na}+\text{K})$ in the white liquor] of 2.4 for inland mills and from 1.1 to 1.6 for West Coast mills. For Finnish mills, Keitanniemi and Virkola reported an enrichment factor of 1.6. For chloride, Reeve et al. (5)

reported an enrichment factor (the ratio of Cl/Na in the fume to Cl/Na in the white liquor) of 3.0 for inland mills and from 1.2 to 1.6 for West Coast mills.

The presence of potassium and chloride in the fume can have a marked effect on the operation of a kraft recovery boiler. Potassium and chlorides significantly lower the melting point of deposits in the kraft furnace. Shivgulam et al. (6) reported the addition of sodium chloride to a synthetic kraft smelt lowered its eutectic melting point from 763 to 598 C. The replacement of 5 mole% sodium with potassium further lowered the eutectic melting point to 525 C. Reeve et al. (5) have attributed severe superheater corrosion to the presence of chlorides and potassium in the fireside deposits. The accelerated corrosion was thought to result from the lower melting point of the enriched deposit.

EQUILIBRIUM TREATMENTS

Several researchers have used thermodynamic equilibrium calculations to predict the liquid and gaseous species present in the kraft furnace. Bauer and Dorland (7) were among the first to apply this technique to the kraft furnace. Their study predicted that the volatile fuming species in the furnace are Na and Na₂. Sodium hydroxide was considered as a liquid species but not as a gaseous species and was predicted not to be present in the melt.

Warnqvist (8) also applied equilibrium thermodynamics to the kraft furnace and concluded that in addition to Na and Na₂, NaOH is also an important fuming compound. Warnqvist recognized that the equilibrium assumption was somewhat unrealistic, but felt that this technique provides a hint of the processes and chemical species present in the furnace.

Recently detailed thermodynamic equilibrium calculations on the inorganics in the kraft furnace have been made by Pejryd and Hupa (9) and Shiang and

Edwards (10). Shiang and Edwards determined that equilibrium calculations predict chloride and potassium enrichment factors greater than 10. They checked these calculations with those of Pejryd and Hupa and found good agreement.

Shiang and Edwards proposed that the lower enrichment factors observed in the kraft furnace result from carryover of black liquor char diluting the chloride and potassium content of the inorganic compounds present in the flue gases. However, there are few carryover particles in the precipitator dust and the chloride and potassium enrichment factors in the precipitator dust range from 1.1 to 3.0. Therefore, carryover dilution is not the cause of the lower than predicted carryover factors.

OXYGEN ENHANCED FUME GENERATION

Work by Clay et al. (11) and Cameron et al. (12) has shown that air oxidation of sodium sulfide in a sodium sulfide/sodium carbonate melt can produce large quantities of sodium carbonate fume. The rate of fume generation under oxidizing conditions was found to be considerably greater than the rate under strongly reducing conditions. This phenomenon was unexpected and very difficult to explain in terms of equilibrium treatments.

Recently, Cameron (13) has shown the large quantity of fume generated during sulfide oxidation is a result of sodium oxidation in the gas phase. Oxidation of sodium vapor near the melt's surface lowers the partial pressure of sodium in the gas phase. Since the driving force for vaporization is the difference between the equilibrium vapor pressure and partial pressure of sodium, this reduction in partial pressure increases the sodium vaporization rate and results in rapid sodium vaporization with only mild reducing conditions in the melt.

This mechanism for fume generation will have a major effect on fume generation in the kraft furnace. Therefore, the fume generation rates within the furnace will be significantly different from those predicted by equilibrium treatments.

OBJECTIVES

The objectives of this research are to compare the relative vaporization processes present in the kraft furnace and to determine the mechanism responsible for the lower than equilibrium predicted potassium and chloride enrichment factors.

EXPERIMENTAL

EXPERIMENTAL SYSTEM

The vaporization experiments were conducted by monitoring the fume produced from alkali carbonate/sulfate/sulfide/chloride melts under various experimental conditions. The experimental system, shown in Figure 1, consisted of an induction heated reactor, gas meters and fume filter. The fume from the reactor was followed by filtering the off-gas and weighing the fume particles. To ensure that this gravimetric method collected all the fume particles in the off-gas, the sodium content of the off-gas after the filter was checked with a flame photometer.

Figure 1 here

The fume particles collected were typically white spherical particles approximately 0.25 to 1.0 μm in diameter. These particles were composed principally of sodium carbonate, potassium carbonate, sodium chloride and potassium chloride.

COMPARISON OF FUME GENERATION RATES UNDER DIFFERENT EXPERIMENTAL CONDITIONS

The equilibrium treatment of fume generation assumes that the large quantity of fume present in the kraft furnace results from the high temperature and reducing conditions present in the furnace bed. The major reducing species present in the kraft furnace are carbon, carbon monoxide, and hydrogen. The fume generation rates were measured with various levels of these reducing species present and compared to rates produced under oxidizing conditions.

Fume Generation Under Oxidizing Conditions

Shown in Table 1 are typical fume generation rates during air oxidation of sodium sulfide in a sodium carbonate/sulfide melt. The origin of fume during sulfide oxidation has been described by Cameron (13) and will not be discussed in detail here. These rates are presented for comparison with fume generation rates under reducing conditions.

Table 1 here

Fume Generation with Carbon Monoxide

To determine if carbon monoxide reduction of sodium carbonate as shown in Eq. (1) is a significant source of fume, a nitrogen gas stream containing 1 to 10% carbon monoxide was bubbled through sodium carbonate/sulfide/sulfate melts. The effect of carbon monoxide on fume generation is shown in Table 2.

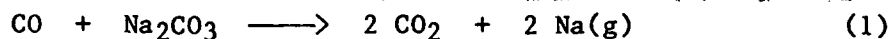


Table 2 here

As shown in this table, carbon monoxide reduction of sodium carbonate is not a mechanism of fume generation. The highest level of fume observed under a carbon monoxide purge was no greater than that observed under a pure nitrogen purge.

Fume Generation with Hydrogen

Hydrogen may react with sodium carbonate to form sodium [Eq. (2)] or sodium hydroxide [Eq. (3)]. Both of these products are volatile and may form fume. To determine if the reaction of hydrogen with sodium carbonate generates fume, a nitrogen stream containing hydrogen was bubbled through sodium carbonate/sulfide/sulfate melts. The fume generation rates from these experiments are shown in Table 3.

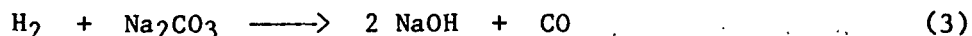
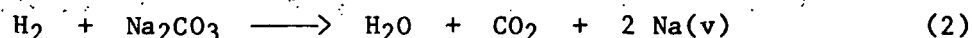


Table 3, here

Although the fume generation rate under a hydrogen purge is greater than that observed under carbon monoxide, it is significantly lower than the levels observed during sulfide oxidation. For example, air oxidation of the sulfide content of these melts would produce an order of magnitude more fume than was observed with hydrogen.

Fume Generation Rates with Carbon

To determine if the reduction of sodium carbonate with carbon [Eq. (4)] is a major source of fume, the fume generation rate was measured with kraft and soda chars present in sodium carbonate/sulfide melts. These chars were obtained from the

pyrolysis of soda and kraft liquors and contain approximately 27% fixed carbon. The fume generation rates resulting from the presence of carbon are shown in Table 4. The carbon levels listed in this table were calculated based on the fixed carbon content of the chars.

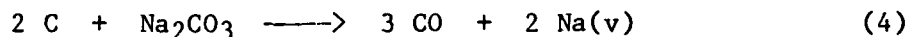


Table 4 here

At the carbon levels used in these melts, the fume generation rate due to the reaction of carbon with sodium carbonate is approximately an order of magnitude lower than the fume generation rate during sulfide oxidation.

Relative to fuming during sulfide oxidation, the reductive mechanisms for fume generation produced only a small level of fume. The presence of carbon monoxide in the purge gas did not produce a detectable increase in the fuming rate. Although hydrogen and carbon did increase fuming relative to nitrogen only, the fuming rates with these species present were significantly lower than those observed during sulfide oxidation.

Fume Generation with Sodium Hydroxide

Equilibrium treatments predict that a major source of fume is the formation and vaporization of sodium hydroxide. To examine this mechanism fume generation was studied with sodium hydroxide pellets added to sodium carbonate/sulfide melts. Table 5 shows the fuming rate from melts with different levels of sodium hydroxide present in the melt.

Table 5 here

As shown in the table, sodium hydroxide is not highly volatile in a sodium carbonate/sulfide melt. Fuming from the melts containing sodium hydroxide with a nitrogen purge was little different from melts containing no sodium hydroxide.

POTASSIUM AND CHLORIDE BEHAVIOR DURING FUME GENERATION

Potassium Behavior during Fume Generation Under Oxidizing Conditions

To determine if fume generated during sulfide oxidation would be enriched in potassium, the potassium/sodium ratio in fume generated during sulfide oxidation was compared to the potassium/sodium ratio in the melt. Shown in Table 6 are the fume generation rates, the potassium/sodium ratio in the fume, and the enrichment factor.

Table 6 here

From this table, it is apparent that the fume generation rate during sulfide oxidation is not highly dependent on the potassium/sodium ratio in the melt and it is also apparent that there is no potassium enrichment in the fume. Therefore, fuming under oxidizing conditions is not the cause of the potassium enrichment in the kraft recovery boiler.

Sodium Chloride Behavior in Sodium Carbonate

The behavior of sodium chloride in sodium carbonate/sulfide melts was studied by adding sodium chloride to sodium carbonate/sulfide melts and monitoring the fume generation rate under both oxidizing and nonoxidizing purges. The chloride/sodium ratios in the melts were chosen to be in the range of typical smelt samples as reported by Reeve et al. (5). The fume samples collected from these

melts were analyzed for sodium and chloride and the enrichment factor then calculated. Table 7 shows the results of these experiments.

Table 7 here

In Run 326, fume was generated with no oxygen in the purge gas. Under these conditions, the fume contained 86% sodium chloride and an enrichment factor of 8.6 was obtained. This enrichment factor compares closely with that of 10 predicted by Shiang and Edwards (10) from equilibrium calculations. Under oxidizing conditions, the rate of sodium vaporization is enhanced by gas phase oxidation of the sodium vapor and the fume enrichment factor is reduced to the area of 1.4 to 1.8, which is near that reported by Reeve et al. (5) for kraft furnaces.

If the vaporization of sodium chloride is an equilibrium process and the melt is an ideal system, the vaporization of sodium chloride may be calculated assuming Raoult's Law [Eq. (6)] and assuming that the gas stream is saturated in sodium chloride.

$$P_{\text{NaCl}}(T) = p^*_{\text{NaCl}}(T) \cdot X_{\text{NaCl}} \quad (6)$$

Here, $P_{\text{NaCl}}(T)$ is the equilibrium partial pressure of NaCl at temperature T; p^*_{NaCl} is the vapor pressure of pure NaCl at temperature T; and X_{NaCl} is the mole fraction of NaCl in the melt.

The vaporization rates for sodium chloride calculated from Raoult's Law are compared to the actual rates calculated from total fume generation rates and fume composition in Table 8.

Table 8 here

As shown in this table, the calculated and measured sodium chloride vaporization rates during sulfide oxidation enhanced fume generation are in close agreement. This indicates that sodium chloride vaporization is an equilibrium process and that its vaporization rate during oxidation enhanced fume generation can be determined assuming Raoult's Law is valid.

Potassium Behavior in Alkali Carbonate/Chloride Melts

With no chloride in the melt, there was no potassium enrichment in the fume during sulfide oxidation. To determine the effect of chloride on potassium enrichment, various levels of potassium chloride and sodium chloride were added to the melt and the fume generated during sulfide oxidation was analyzed for potassium and chloride. The results of these experiments are shown in Table 9.

Table 9 here

As shown in Table 9, the addition of potassium chloride to the melt results in the fume generated during sulfide oxidation being enriched in both potassium and chloride. As previously shown in Table 6, no potassium enrichment was observed when the only potassium species present in the melt were potassium carbonate and potassium sulfide. Therefore, the potassium enrichment observed in the fume is due to the presence of potassium chloride in the melt.

To determine if Raoult's Law describes potassium chloride vaporization during sulfide oxidation fume generation, the potassium and chloride enrichment factors were calculated based on Raoult's Law and compared to the observed enrichment factors. These calculations are shown in Table 10.

Table 10 here

It was previously shown that with no chlorides in the melt no potassium enrichment occurred in fume generated during sulfide oxidation. Since the carbonate portion of the fume in Table 10 results from gas phase oxidation enhanced vaporization, no potassium enrichment should occur in this portion of the fume. Therefore, potassium enrichment factors in Table 10 were calculated assuming that all potassium enrichment resulted from potassium chloride vaporization. The calculated potassium enrichment factor is significantly lower than the observed enrichment factor. This difference results from either potassium chloride having an activity coefficient much greater than one, or from the carbonate portion of the fume also being enriched in potassium due to the presence of potassium chloride in the melt.

Although the sodium and potassium chloride vaporization are responsible for the chloride and potassium enrichment observed in fume generated during sulfide oxidation, the vaporization of these species contributes little total fuming rate. For example, in Table 10 less than 20% of the total potassium and sodium in the fume results from the vaporization of the chlorides. The majority of the fume generated is a result of oxidation enhanced vaporization of sodium and potassium.

DISCUSSION

In the study of different fuming mechanisms, it is apparent that the fume generation during sulfide oxidation is considerably greater than under strongly reducing conditions. For example, the highest fuming rate observed under reducing conditions was with the presence of carbon in the melt, and under these conditions the maximum rate was 0.0008 mole of sodium carbonate fume per mole of off-gas. During sulfide oxidation the fuming rate is nearly an order of magnitude greater than this rate.

One mechanism that has been proposed for fume generation in the kraft furnace is the formation and vaporization of sodium hydroxide. The vaporization of sodium hydroxide was studied by adding sodium hydroxide to the alkali carbonate-sulfide melts and measuring the fuming rate. In these experiments, relatively high levels of sodium hydroxide were added to the melt and no increase in fume generation was observed. Sodium hydroxide is also formed in the melt when hydrogen is present in the gas phase and, although significant quantities of carbon monoxide were evolved during the hydrogen reducing experiments (indicating the formation of sodium hydroxide), no increase in fume generation was observed. Therefore, sodium hydroxide is not highly volatile in an alkali carbonate-sulfide melt and is not likely a major source of fume in the kraft furnace.

One of the major areas of interest in the kraft furnace is the behavior of the potassium and chloride compounds. Equilibrium calculations on the vaporization rates in the furnace predict a chloride enrichment factor considerably greater than that actually observed. The experimental results presented in this study demonstrate that oxidation enhanced vaporization of sodium can reduce the enrichment factor for chloride to that observed within the kraft furnace. Oxidation enhanced vaporization of sodium is then the likely mechanism that results in the significantly lower than predicted chloride enrichment factor.

The experimental results on sodium chloride vaporization demonstrate that sodium chloride can be treated as an ideal system and that the sodium chloride vaporization rates during oxidation enhanced fume generation can be predicted by assuming Raoult's Law is applicable.

No potassium enrichment was observed during oxidation enhanced fume generation when chlorides were not present in the melt. When chlorides were present

in the melt, the fume was enriched in potassium and the enrichment factors were similar to those observed in the kraft furnace. Therefore, the potassium enrichment observed in the kraft furnace is likely a result of the presence of chloride.

REFERENCES CITED

1. Borg, A.; Teder, A.; Warnqvist, B., Tappi 57(1): 126-9(Jan., 1974).
2. Rzhinshvile, G. V.; Kaplun, L. V., Bumazh. Prom. (1): 26-8(Jan., 1983).
3. Keitanniemi, O.; Virkola, N. E., Paperi Puu (9): 507-22(1978).
4. Karjalainen, P. O.; Lojkrantz, J. E.; Christie, R. D., Pulp Paper Can. (12): 95-101(Dec., 1972).
5. Reeve, R. W.; Tran, N. T.; Barham, D., Tappi 64(5):109-13(May, 1981).
6. Shivgulam, N.; Barham, D.; Rapson W. H., Pulp Paper Can. 80(9): T282-5 (Sept., 1979).
7. Bauer, T. W.; Dorland, R. M., Can. J. Technol. 32: 91(1954).
8. Warnqvist, B., Svensk Papperstid. 76(12): 463-6(1973).
9. Pejryd, L.; Hupa, M. "Bed and Furnace Gas Composition in Recovery Boilers." 1984 TAPPI Pulping Conference, San Francisco.
10. Shiang, N.; Edwards, L. "Understanding and Controlling Fireside Deposits in Kraft Recovery Furnaces." AIChE Summer Meeting, Boston, Aug. 1986.
11. Clay, D. T.; Grace, T. M.; Kapheim, R. J., AIChE Symposium Series 239: 80, 99(1984).
12. Cameron, J. H.; Clay, D. T.; Grace, T. M. "Oxidative Fuming - the Phenomenon and Possible Interpretations." International Conference on Recovery of Pulping Chemicals, April, 1985.
13. Cameron, J. H. "Reaction Enhanced Vaporization of Molten Salt." In Press, Chemical Engineering Communications, 1986.

Table 1. Typical Fume Generation Rates during Sulfide Oxidation

Initial Melt Composition

Na_2CO_3 = 0.77 mole

Purge = 1.15 L/min at 13.0% O_2

Na_2S = 0.06 mole

Temperature = 954 C

Time, s	Calculated Concentrations		Fume Generation Rate, g/min	Fume/Off-Gas Mole Na_2CO_3 / Mole N_2
	Na_2SO_4 mole/L	Na_2S mole/L		
191	0.010	0.049	0.0212	0.0043
278	0.015	0.044	0.0212	0.0043
452	0.025	0.035	0.0225	0.0046
627	0.035	0.025	0.0239	0.0049
738	0.041	0.019	0.0245	0.0050
933	0.052	0.008	0.0241	0.0049

Table 2. Fume Generation with Carbon Monoxide

Initial Melt Composition

Na_2CO_3 = 0.77 mole

N_2 Purge = 1.0 L/min

Na_2S = 0.03 mole

CO = 0.0 to 0.1 L/min

Na_2SO_4 = 0.0 to 0.02 mole

Temperature = 954 C

Na_2SO_4 Added, mole	Purge Rate		Fume Generation Rate, g/min	Fume/ N_2 Mole Na_2CO_3 / Mole N_2
	N_2 L/min	CO L/min		
0.0	1.0	0.0	0.00076	0.00016
0.0	0.98	0.01	0.00036	0.00008
0.0	0.98	0.03	0.00076	0.00016
0.0	0.98	0.05	0.0008	0.00017
0.0	0.98	0.1	0.00072	0.00015
0.01	0.98	0.1	0.0	0.0
0.02	0.98	0.1	0.00016	0.00003

Table 3. The Effect of Hydrogen on Fume Generation

Initial Melt Composition

Na_2CO_3 = 0.77 mole

Na_2S = 0.03 mole

Na_2SO_4 = 0.0 to 0.03

Temperature = 954 C

Purge

N_2 = 1.0 L/min

H_2 = 0.0 to 0.1 L/min

Na_2SO_4 Added, mole	Purge Rate		Fume Generation Rate, g/min	Fume/ N_2 Mole Na_2CO_3 / Mole N_2
	N_2 L/min	H_2 L/min		
0.0	1.0	0.0	0.00076	0.00016
0.0	0.92	0.02	0.0007	0.00016
0.0	0.92	0.05	0.0008	0.00018
0.0	0.92	0.1	0.002	0.00046
0.03	0.92	0.1	0.002	0.00046

Table 4. Fume Generation in the Presence of Carbon

Initial Melt Composition

Purge

$\text{Na}_2\text{CO}_3 = 0.77$

$\text{N}_2 = 1.0 \text{ L/min}$

$\text{Na}_2\text{S} = 0.03$

Temperature = 954 C

Carbon Added, mole	Purge Rate N_2 , L/min	Fume Generation, g/min	Fume/Off-Gas mole Na_2CO_3 / mole N_2
0.016, S	1.0	0.0012	0.00025
0.032, S	1.0	0.0039	0.00082
0.016, K	1.0	0.002	0.00042
0.032, K	1.0	0.0025	0.00053

S = Soda Char, K = Kraft Char.

Table 5. Effect of Sodium Hydroxide on Fume Generation

Melt Composition

Na₂CO₃ = 0.77 mole

Na₂S = 0.0 to 0.03 mole

NaOH = 0.0 to 0.1 mole

Purge

N₂ = 1.0 L/min

Temperature = 954 C

Na ₂ S Added, mole	NaOH Added, mole	Fume Generation Rate, g/min	Fume/Off-Gas mole Na ₂ CO ₃ / mole N ₂
0.0	0.012	0.0	0.0
0.0	0.031	0.0	0.0
0.03	0.0	0.00076	0.00016
0.03	0.01	0.0007	0.00015
0.03	0.10	0.0007	0.00016

Table 6. Potassium Behavior during Fume Generation under Oxidizing Conditions

Temperature = 954 C

O₂ Flow Rate = 0.021 L/min

N₂ Flow Rate = 1.0 L/min

Initial Melt Composition				Fume Generation, g/min	Fume K/Na Molar Ratio	Enrichment Factor
Na ₂ CO ₃ , mole	K ₂ CO ₃ , mole	Na ₂ S mole	K/Na Molar Ratio			
0.75	0.02	0.03	0.0256	0.075	0.0225	0.88
0.71	0.06	0.03	0.0811	0.0765	0.0888	1.09
0.67	0.1	0.03	0.143	0.0683	0.141	0.99
0.37	0.4	0.03	1.0	0.058	0.96	0.96
0.1	0.71	0.03	5.46	0.053	6.01	1.10

Table 7. Chloride Enrichment from Carbonate Melts

Melt Composition		Purge Rate
Na ₂ CO ₃	= 0.575 to 0.62 mole	N ₂ = 1.0 L/min
Na ₂ S	= 0.143 to 0.16 mole	O ₂ = 0.0 to 0.1 L/min
NaCl	= 0.10 to 0.20 mole	
Temperature = 954 to 982 C		

Run No.	Temp., C	Melt Cl/Na Molar Ratio	O ₂ Flow Rate, L/min	Fume Cl/Na Molar Ratio	Enrichment Factor
326	954	0.10	0.0	0.86	8.6
327	954	0.049	0.1	0.0815	1.66
328	982	0.049	0.1	0.0759	1.55
329	954	0.122	0.1	0.221	1.81
330	982	0.122	0.1	0.175	1.43

Table 8. Calculated and Measured Vaporization Rates of Sodium Chloride during Sulfide Oxidation in a Carbonate Melt

Run No.	Total Fume Generation, g/min	Cl Content of Fume, wt. %	Calculated NaCl Vaporization, g/min	Measured NaCl Vaporization, g/min
327	0.0146	5.34	0.0012	0.00128
328	0.0193	4.95	0.00217	0.00158
329	0.0162	14.1	0.0031	0.00376
330	0.02485	11.5	0.00462	0.00471

Table 9. Effect of Chloride on Potassium Enrichment during Sulfide Oxidation

Melt Composition

Purge Rate

Na_2CO_3 = 0.565 mole

N_2 = 1.0 L/min

Na_2S = 0.14 mole

O_2 = 0.0 to 0.1 L/min

NaCl = 0.1 to 0.16 mole

KCl = 0.02 to 0.10 mole

Temperature 954 C

Run No.	Melt		O_2 Flow Rate, L/min	Fume		Enrichment Factor	
	Cl (Na+K)	K (Na+K)		Cl (Na+K)	K (Na+K)	Cl	K
343	0.119	0.0187	0.0	0.745	0.119	6.3	6.8
331	0.122	0.062	0.1	0.164	0.10	1.3	1.6
344	0.119	0.0188	0.1	0.173	0.046	1.5	2.4
345	0.127	0.0278	0.1	0.16	0.051	1.3	1.9
346	0.116	0.0129	0.1	0.19	0.026	1.5	2.0

Table 10. Potassium and Chloride Enrichment Factors

Run No.	Calculated Enrichment Factors		Observed Enrichment Factors	
	Cl	K	Cl	K
331	1.6	1.2	1.3	1.6
344	1.3	1.2	1.5	2.4
345	1.3	1.2	1.3	1.9
346	1.3	1.2	1.5	2.0

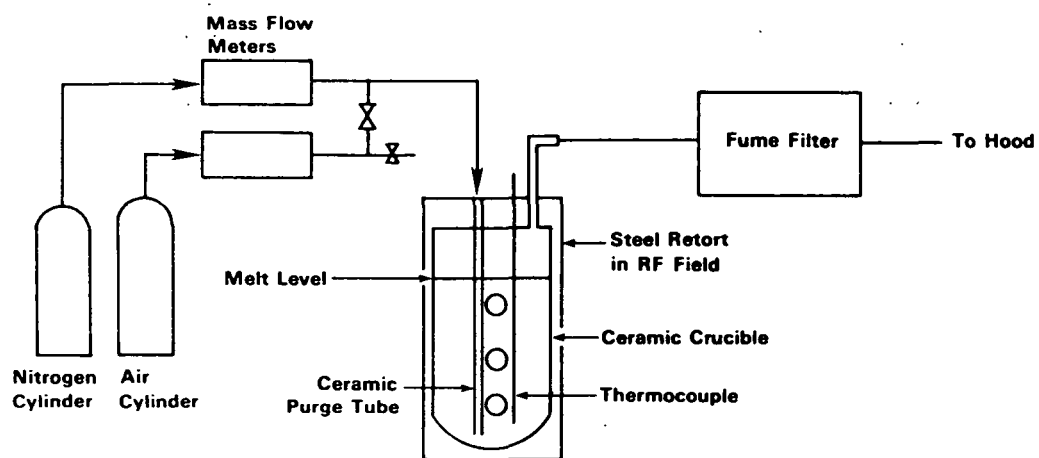


Figure 1. Experimental System